

# X-ray Diffraction on Unprepared Rock Samples: A Study of Sulphate Minerals

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## 1. Back-Reflection X-Ray Diffraction

Conventional angle-dispersive X-Ray Diffraction (ADXRD) utilises the Bragg equation:

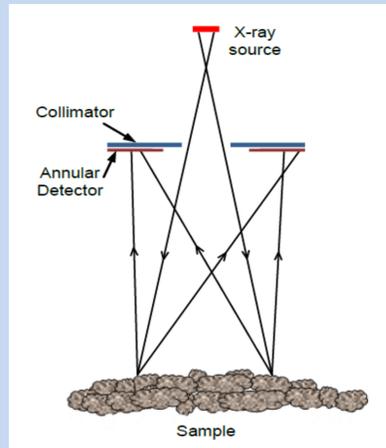
$$\lambda = 2d \sin\theta$$

by scanning through a range of  $2\theta$  scattering angles with a monochromatic X-ray source to determine the  $d$ -spacing of the crystal planes, which are characteristic of each mineral phase. This means that XRD can be used for mineral identification, quantification and structural analysis. An alternative approach to XRD is to use a fixed geometry and a broadband X-ray source with an energy resolving detector. This approach is known as Energy-Dispersive XRD (EDXRD), and the Bragg equation can be rewritten as:

$$Ed \sin\theta = 6.199 \text{ keV \AA}$$

This study uses an energy-dispersive XRD technique in a novel back-reflection geometry ( $2\theta \approx 180^\circ$ ) that proof-of-principle experiments have shown to be uniquely insensitive to sample morphology, allowing the analysis of unprepared rock samples, and only intensity-dependent with regards to sample-instrument distance [1-3]. In contrast, conventional XRD techniques require the sample to be crushed into a fine powder and be presented to the instrument for analysis with a uniformly flat surface, with sub-millimetre position accuracy.

Conventional ADXRD typically scans through the range  $2\theta = 5 - 90^\circ$  using Cu-K $\alpha$  radiation, corresponding to the  $d$ -spacing range 17.67 – 1.09 Å, which in the back-reflection geometry corresponds to 0.35 – 5.7 keV. However, this energy range has a significant overlap with the fluorescence of common rock-forming elements: O, Na, Mg, Al, Si, K, Ca and Ti. This can be overcome by the suppression of fluorescence peaks, as described in [4]. A disadvantage of the technique is the low resolution of diffraction peaks at this geometry. [1]



The back-reflection technique can be utilised to return the diffraction and fluorescence data of a sample revealing complementary mineralogical and elemental information of a sample. Another advantage of the fixed back-reflection geometry of this technique is that it lends itself to a compact, lightweight instrument design and is therefore of interest for planetary science missions where strict mass, power and volume budgets are imposed on instrumentation [2].

Figure 1: Diagram showing the novel back-reflection EDXRD geometry [2].

## 2. Sulphate Minerals and Mars

The study of sulphate minerals is of particular interest in planetary science as they can form from the evaporation of a body of standing water or groundwater [5,6]. The identification of sulphate minerals such as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ) is important in order to characterise fluid composition and temperature of ancient aqueous activity. Sulphates have been identified on Mars both in-situ with the Curiosity rover [7] and Mars Exploration Rovers [8] and remotely using the Compact Reconnaissance Imaging Spectrometer for Mars on-board Mars Reconnaissance Orbiter [9].

Analogues of Yellowknife Bay, Gale Crater, Mars were collected from the Triassic Coast at Watchet Bay, Somerset, UK [10] with the aim of testing the capability of the back-reflection technique, and to subsequently compare analysis with vein formation at the Mars Science Laboratory site on Mars.

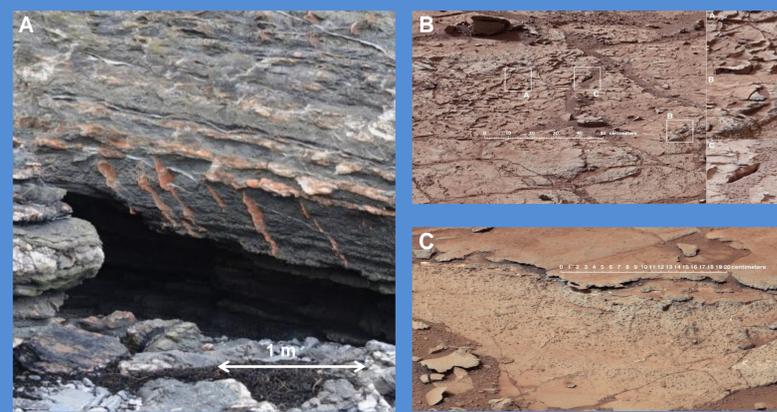


Figure 2: A: Image of Watchet Bay, Somerset UK. B and C: Images of Yellowknife Bay, Gale Crater, Mars (Credit: Mars Science Laboratory, NASA).

## 4. Conclusions

This work demonstrates the capability of a novel ED-XRD technique in a back-reflection geometry. Together with PoDFluX, this technique is capable of identifying sulphate and Fe-oxide minerals, overcoming the effects of XRF peaks that overlap XRD peaks and also the effects of preferred orientation. This demonstrates the potential of an instrument based on this technique, and its potential use on the arm of a rover or lander deployed on a planet, such as Mars.

## 3. Samples and Spectra

The laboratory facility outlined in [3] was used to carry out experiments on prepared pressed-powder pellet samples and unprepared whole rock samples from Watchet Bay. Fluorescence peaks overlapping the diffraction peaks were identified and a process of suppressing these peaks by tuning the source excitation voltage was carried out to reveal the underlying diffraction data. Figure 3 shows sulphur-fluorescence suppression results for a whole rock sample. The experimentally acquired data is compared to an XRD/XRF model of gypsum produced by PoDFluX [11] using data from [12], with a specified preferred orientation effect along the (010) plane [13]. Magnesium, Aluminium and Silicon XRF are also included in the model.

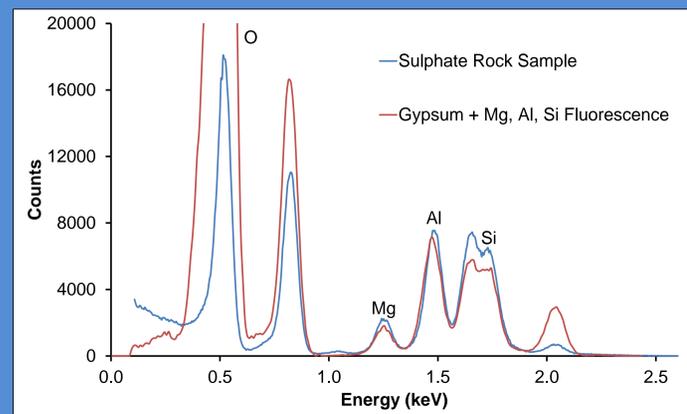
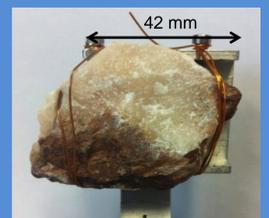


Figure 3: Left: Experimentally acquired spectrum of the sulphate rock sample compared to a model of gypsum with preferred orientation effects along the (010) plane, and Mg, Al, Si fluorescence. Below: Whole rock sample attached to sample holder.



The whole rock sample spectrum shows more peaks due to Mg, Al, Si XRF, and including this with a model of gypsum explained the data well.

Using a bespoke back-reflection setup, comprising of an approximately annular 4-channel silicon drift detector centered on the incident x-ray beam as illustrated in figure 1, measurements have been taken to further assess the capability of the technique. Figure 4 shows calcium-suppression results for a whole rock sample, which was broken off from the sulphate sample pictured in figure 3. An XRD model of gypsum produced by PoDFluX [11] is also shown in figure 4 for comparison.

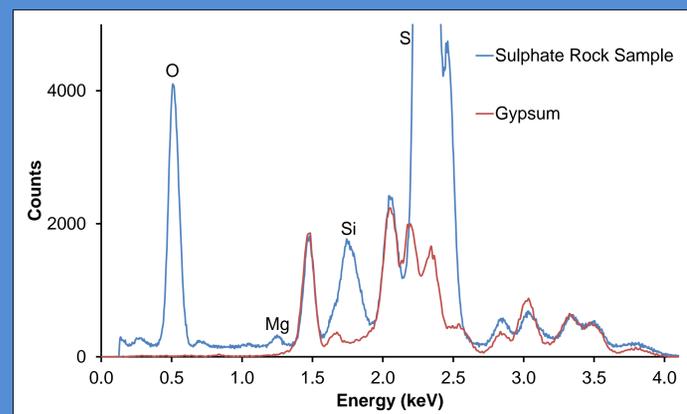


Figure 4: Left: Experimentally acquired spectrum of the sulphate rock sample compared to a Monte Carlo ray tracing simulation of gypsum. Below: Whole rock sample.



The sulphate sample shown in figures 3 and 4 was also analysed using a standard powder ADXRD technique with a Bruker D8 Advance, in the Department of Geology at the University of Leicester. Using this technique it was determined that gypsum was the dominant mineral, reaffirming the result obtained using the novel back-reflection technique.

In addition to the sulphate study shown here, the bespoke back-reflection setup has been used to analyse multiple samples. Figure 5 shows iron-suppression results for a whole rock sample of hematite, of unknown origin (donated by the Department of Geology at the University of Leicester). An XRD/XRF model of hematite produced by PoDFluX [11] using data from [14] is also shown in figure 5, with a specified preferred orientation effect along the (001) plane [13] and Rayleigh scattering effects. Oxygen, aluminium, silicon, zirconium and sulphur XRF are also included in the model. Zirconium XRF is due to an instrument artefact. The model in figure 5 gives extremely good agreement, explaining all the peaks in the spectrum but underestimates Rayleigh scattering at low energies resulting in an  $\sim 0.93$  keV peak,

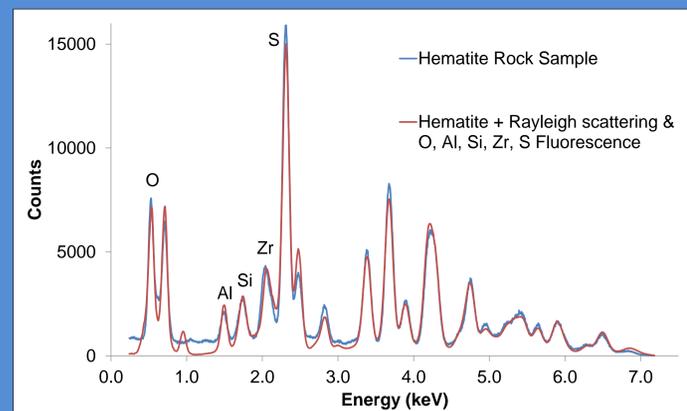


Figure 5: Left: Experimentally acquired spectrum of the hematite rock sample compared to a Monte Carlo ray tracing simulation of hematite with preferred orientation effects along the (001) plane, Rayleigh scattering effects and O, Al, Si, Zr and S fluorescence. Below: Whole rock sample.



## References

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